

Catalytic Transfer Hydrogenation of Biomass-Derived Ethyl Levulinate into Gamma-Valerolactone Over Graphene Oxide-Supported Zirconia Catalysts

Jinhua Lai¹ · Shuolin Zhou¹ · Xianxiang Liu¹ · Yongjun Yang² · Jing Lei² · Qiong Xu¹ · Dulin Yin¹

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Abstract

The transformation of biomass-derived intermediates into value-added chemicals and liquid fuels is of great importance in sustainable chemistry. In this study, graphene oxide supported ZrO_2 (ZrO_2/GO) was found to be an active heterogeneous catalyst for the transfer hydrogenation of ethyl levulinate to γ -valerolactone (GVL) with *iso*-propanol as the hydrogen donor. Several important reaction parameters such as the hydrogen donor, the reaction temperature and the catalyst loading were studied in detail with the aim to get a high yield of GVL. It was found that the structure of alcohols had a great effect towards the activity of the ZrO_2/GO catalyst and the selectivity of GVL. *Iso*-propanol was the best hydrogen donor for the transfer hydrogenation of ethyl levulinate to GVL. The highest GVL yield reached 91.7% with an ethyl levulinate conversion of 96.2% under optimal reaction conditions. More importantly, the ZrO_2/GO catalyst demonstrated a high stability without the loss of its catalytic activity during the recycling experiments, which should be due to the strong interaction between GO and ZrO_2 .

Graphical Abstract

The graphene oxide supported ZrO_2 (ZrO_2/GO) catalyst showed high activity for the transfer hydrogenation of ethyl levulinate to GVL with a high yield up to 91.7%.



Keywords Non-noble metal catalyst \cdot Transfer hydrogenation reaction \cdot Ethyl levulinate $\cdot \gamma$ -Valerolactone \cdot Sustainable chemistry

Jinhua Lai and Shuolin Zhou contributed equally to this work.

Xianxiang Liu lxx@hunnu.edu.cn

Extended author information available on the last page of the article

1 Introduction

The gradual depletion of fossil fuel resources has forced the world to seek new routes for the production of chemicals and fuels from the renewable resources [1]. In contrast to other renewable resources, the non-food biomass is the only carbon-containing renewable resources, which can provide

both chemicals and fuels to the world [2, 3]. Therefore, great attention has been paid to the development of the effective methods for the transformation of biomass into biofuels and value-added chemicals, which has emerged as one of the promising ways to alleviate the current reliance on fossil fuel sources [4, 5].

Through careful design of catalytic systems, many kinds of important chemicals as well as the liquid fuels have been successfully derived from biomass resources [6]. Among them, there has been a growing attention on the synthesis of γ -valerolactone (GVL), owing to its versatile application in many fields [7]. GVL has been identified as a green and renewable solvent for chemicals reaction, and it was reported that GVL sometimes could improve the performance of biomass conversion and organic transformations in terms of the catalytic efficiency as well as the product purification [8, 9]. GVL can be used as an additive suitable for liquid fuels, perfumes, and food [7]. More importantly, GVL can serve as the intermediate for the production of gasoline and diesel fuels (e.g., C8-C18 alkanes and 2-methyltetrahydrofuran) and valuable chemicals, such as 1,4-pentanediol, methyl pentenoate [10], and ionic liquids [11]. Owing to the wide application of GVL, the synthesis of GVL from renewable carbohydrates or the biomass-derived chemicals have been extensively studied in recent years [12–14]. The direct and simple way to produce GVL is the hydrogenation of levulinic acid (LA) and its esters, which can be readily synthesized from lignocellulosic biomass through multiple catalytic steps in the presence of acid catalysts. However, the hydrogenation step posed a challenge to researchers with the combined effect of the carbonyl and ester groups on selective hydrogenation.

The catalytic reduction of levulinic acid and its esters have been generally been performed in the presence of metal catalysts, especially noble metal catalysts by the use of hydrogen [15, 16]. Although hydrogen is a clean hydrogen source, these catalytic systems demonstrated some drawbacks such as the low solubility of molecular hydrogen in most solvents, the need of high pressure, the use of expensive noble metal catalyst, and the low stability of the metal catalyst. For example, Yang et al. prepared porous carbon nanofibers encapsulated Ru nanoparticles for the transfer hydrogenation of LA into GVL, which was performed at 150 °C and 45 bar H₂ pressure [17].

In recent years, catalytic reactions with other hydrogen donors such as formic acid and alcohols instead of hydrogen have received much interest [18]. This process can avoid the use of explosive hydrogen; thus, it seems to be more economical and much safer. In the process of the transfer hydrogenation of levulinic acid and its esters into GVL, the hydrogen donors were mainly used formic acid and alcohols. It is highly attractive to perform the transfer hydrogenation with formic acid, as it is also renewable from carbohydrates.

Synthesis of GVL from levulinic acid and its ester via the use of formic acid as the hydrogen donor was generally performed over noble metal catalysts such as Au and Ru catalysts [19]. Obviously, the use of noble metals and the corrodibility of formic acid under harsh conditions have limited the application of formic acid for the transfer hydrogenation of levulinic acid and its ester. Compared with formic acid, the use of alcohols as the hydrogen source for the transfer hydrogenation of levulinic acid and its ester into GVL has received much more attention in recent years. Up to now, several catalytic systems have been developed for the transfer hydrogenation reactions of levulinic acid and its esters to GVL using various alcohols as the hydrogen source, including homogeneous Ru complexes, RANEY®Ni, and Lewis acids especially Zr based catalysts [20, 21]. However, some drawbacks still need to overcome, such as harsh reaction temperatures, long reaction time, low catalyst reactivity and stability. Therefore, the development of new efficient and cost-effective methods for the production of GVL is a highly attractive task.

Herein we reported the synthesis and characterization of a graphene oxide supported ZrO_2 catalyst (ZrO_2/GO), containing Lewis acidic zirconium sites and Bronsted acidic carboxyl and hydroxyl groups, under hydrothermal method. The as-synthesized ZrO_2/GO catalyst showed high catalytic activity in the transfer hydrogenation of ethyl levulinate into GVL. Obviously, our developed methods demonstrated some advantages such as the use of easily preparative non-noble metal catalyst with low cost, and did not use the explosive hydrogen.

2 Experimental Section

2.1 Materials and Methods

All other chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemicals and solvents were used directly without purification.

2.2 Catalyst Preparation

Graphene oxide (GO) was prepared by a modified Hummer's method [22]. Briefly, graphite, NaNO₃ and 98.0 wt% H_2SO_4 were firstly stirred at 0 °C for 30 min. Then KMnO₄ was added into the mixture slowly and the mixture was continuously stirred at 0 °C for 2 h. After the addition of KMnO₄, the mixture was stirred for 2 h at 0 °C, subsequently at 25 °C for 5 days. After that, 98 wt% H_2SO_4 was added dropwise and then stirred at 98 °C for 2 h. The temperature was then reduced to 25 °C and the mixture was stirred for another

2 h. Then, the solid product was collected by centrifugation, and washed with 3 wt% H_2SO_4 and 3 wt% HCl. Finally, the solid product was dried in a vacuum oven at 40 °C to obtain graphite oxide.

The ZrO_2/GO catalyst was prepared via hydrothermal methods. 150 mg of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 50 mL of water and 1 g of GO support was slowly added into the $ZrOCl_2$ solution with continuous stirring for 30 min. The mixture was then transferred into a 100 mL Teflon-lined stainless steel reactor which was heated at 160 °C for 12 h in a muffle furnace. Upon heating for the set time, the reactor was cooled down to room temperature and the material was filtered to obtain solid powder. The filtered material was subsequently washed with water and alcohol, and dried at 80 °C in a vacuum oven overnight. The as-synthesized material was denoted as ZrO_2/GO .

2.3 Catalyst Characterization

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G²-20 instrument. The sample powder was firstly dispersed in ethanol and dropped onto copper grids for observation. X-ray powder diffraction patterns of samples were determined with a Bruker advanced D8 powder diffractometer (Cu Ka). The scan ranges were 10°-80° with 0.016° steps, respectively. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Ka source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. UV-Visible absorption spectra and the molecular absorption spectra were recorded on a Shimadzu ultraviolet and visible spectrophotometer (Kyoto, Japan).

2.4 General Procedure of the Transfer Hydrogenation of Ethyl Levulinate into GVL

The transfer hydrogenation of ethyl levulinate into GVL was performed in a stainless steel 40 mL Parr batch reactor. A representative procedure was as follows: ethyl levulinate (1 mmol), ZrO_2/GO (40 mg) catalyst and *iso*-propanol (10 mL) were charged in the reactor. The air in the reactor was exchanged with nitrogen for five times and sealed under N₂ pressure (1.0 MPa). Then the autoclave was heated from room temperature to 180 °C within 10 min and then the reactor to room temperature, the reaction mixture was filtrated, and the clear solution was analyzed by gas chromatography.

2.5 Recycling of the Catalyst

After reaction, the ZrO_2/GO catalyst was collected by an external magnet and it was washed with water and ethanol for three times, respectively. Then it was dried at 100 °C over night. The spent catalyst was reused for the next time under the same identical condition as the first run. These processes were repeated for five times.

3 Results and Discussion

The ZrO_2/GO catalyst was prepared via hydrothermal methods in the presence of GO. During the hydrothermal process, $ZrOCl_2 \cdot 8H_2O$ was transformed into ZrO_2 , which was then deposited on the surface of the GO support. The heterostructure of the ZrO_2/GO catalyst can be verified by the morphological analyses. Figure 1 shows the typical TEM images of graphite oxide and the as-prepared $ZrO_2/$ GO catalyst. ZrO_2 particles was clearly observed on the surface of the GO support, and no ZrO_2 particles are scattered out of the GO support, which indicates that there exists a





strong interaction between ZrO_2 particles and the support. The strong interaction between the ZrO_2 particles and the GO support should be possibly derived by the interaction between the oxygen-containing functional groups such as hydroxyl group and carboxylic acid groups on the surface of the GO and the ZrO_2 particles [23]. The TEM results clearly indicates that this method is effective for the preparation of GO supported ZrO_2 particles. However, ZrO_2 particles were observed to have a wide size distribution. The enlarged TEM image of the ZrO_2/GO catalyst in Fig. 1 shows ZrO_2 particles are almost in an oval morphology, and the large ZrO_2 particle was composed of the small-sized nanoparticles with dark dots. On the other hand, graphene oxide has a layer structure, which is believed to be composed of many individual sheets [24].

To obtain insights into the local structure of Zr species supported on the surface of GO, X-ray diffraction (XRD) of the ZrO₂/GO catalyst were performed. In the XRD patterns of the ZrO₂/GO catalyst (Fig. 2), a strong peak at $2\theta = 24.8^{\circ}$ was present in the XRD spectrum of the ZrO₂/GO catalyst, and this peak was assigned to the (002) plane of graphite carbon, which was the characteristic peak of the graphite structure [22]. In addition, a weak peak at $2\theta = 43.7$ suggests the formation of intralayer condensation for the carbon materials in the graphite layers [22]. As far as the crystal structure of ZrO₂, it has three phases including tetragonal phase, cubic phase, and monoclinic phase. Besides the characteristic peaks of the GO, three peaks with a weak intensity at $2\theta = 30.3^{\circ}$, 31.5° , 34.8° and 50.3° were attributed to the XRD peaks of the monoclinic phase (JCPDS NO. 37-1484) [24, 25].

The valence state of the ZrO_2/GO catalyst was further characterized by XPS. As shown in the survey scan spectrum of the ZrO_2/GO catalyst Fig. 3a, these peaks are corresponded to the binding energy of Zr, C and O, which indicates that the ZrO_2/GO catalyst is composed of the



Fig. 2 XRD patterns of the GO/ZrO₂ catalyst



Fig. 3 XPS survey scan spectrum of the ZrO_2/GO catalyst (a), and the XPS spectrum of the Zr 3d in the ZrO_2/GO catalyst (b)

three elements of Zr, C and O without no impurity such as Cl. In addition, the Zr 3d peaks in Fig. 3b can be fitted into two peaks with the binding energies at 182.7 eV and 184.9 eV, which were the characteristic binding energy of Zr^{4+} [24]. Thus, the XPS results also revealed that ZrO_2 was successfully formed by the hydrothermal treatment of $ZrOCl_2 \cdot 8H_2O$, and loaded on the surface of the GO support.

Diffuse reflectance UV–Vis spectra of the ZrO_2/GO catalyst and the GO support were shown in Fig. 4. The GO support showed no distinct absorption peak in the UV–Vis region. However, after loading the ZrO_2 particles on the surface of the GO, there exists two distinct peaks in the UV region for the ZrO_2/GO catalyst. The broad absorption band around 205–250 nm due to the ligand-to-metal charge transfer from an O^{2-} to Zr^{4+} ion of highly dispersed Zr^{4+} in an isolated tetrahedral configuration [24]. Further a distinct absorption band at 280–410 nm can be attributed to the well dispersed ZrO_2 nanoparticles [24, 25]. These results confirmed the presence of highly dispersed ZrO_2 species in ZrO_2/GO catalysts.



Fig. 4 Diffuse reflectance UV–Vis spectra of the samples

3.1 Catalytic Transfer Hydrogenation of Ethyl Levulinate with Different Kinds of Alcohols

Firstly, the transfer hydrogenation of ethyl levulinate into GVL was studied over the ZrO₂/GO catalyst with different hydrogen donors, and the results are listed in Table 1. The reactions were performed at 180 °C with the hydrogen donors as the reaction solvents. It was observed that the structure of the hydrogen donors showed a great effect on the conversion of ethyl levulinate as well as the selectivity of GVL. When the reaction was performed in methanol, there was no aim product of GVL (Table 1, Entry 1). However, a relative high ethyl levulinate conversion of 65.7% was observed in methanol (Table 1, Entry 1). Methyl levulinate was observed to be the byproduct, which was formed via the transesterification of ethyl levulinate with methanol. A low conversion of ethyl levulinate was observed in ethanol, but GVL was obtained with the highest selectivity of 98.6% (Table 1, Entry 2). The highest selectivity of GVL in ethanol was due to the fact that the there was no transesterification of ethyl levulinate in ethanol (Table 1, Entry 2). In addition, it also demonstrated

 Table 1
 The catalytic transfer

 hydrogenation of ethyl
 levulinate over different

 hydrogen donors
 hydrogen donors

that GVL was stable at the reaction temperature of 180 °C. When the reaction was performed in *n*-propanol, the conversion of ethyl levulinate increased to 28.3% in comparison with ethanol (Table 1, Entry 3). However, the selectivity of GVL in *n*-propanol decreased to 59.4% (Table 1, Entry 3). The main byproduct was *n*-propyl levulinate, which was also generated by the transesterification of ethyl levulinate with *n*-propanol. These results in Entries 1–3 revealed that the transesterification of ethyl levulinate became much more difficult for the alcohols with an increase of the carbon atoms due to the increase of the steric hindrance. Meanwhile, the transfer hydrogenation ability increased in an order of methanol, ethanol, and *n*-propanol.

As shown in Table 1, a high ethyl levulinate conversion of 63.2% and a high GVL selectivity of 92.7% were obtained when the reaction was performed in iso-propanol over the ZrO₂/GO catalyst (Table 1, Entry 4). Compared the results between the use of *n*-propanol and *iso*-propanol, the side reaction of the transesterification of ethyl levulinate was greatly inhibited, which was due to the large steric hindrance of iso-propanol. Meanwhile, the high conversion of ethyl levulinate by the use of iso-propanol as the hydrogen donor indicated that the secondary alcohol (isopropanol) was much more active than the primary alcohols as a hydrogen donor for the transfer hydrogenation, possibly due to it giving a high stability intermediate after release of the hydrogen atoms. Acetone as the dehydrogenation product was also determined, and its content was equal to the amount of GVL. However, iso-butanol with a similar structure of iso-propanol produced a lower conversion of ethyl levulinate, but with a slight higher selectivity of GVL due to its larger steric hindrance in comparison with iso-butanol (Table 1, Entry 5). As expected, no conversion of ethyl levulinate was observed when the transfer hydrogenation of ethyl levulinate was conducted with tert-butanol as the hydrogen donor (Table 1, Entry 6). The reason should be that there was no hydrogen close to the hydroxyl group in tert-butanol to produce the

Entry	Hydrogen donors	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	Methanol	ZrO ₂ /GO	5.7	0	0
2	Ethanol	ZrO ₂ /GO	7.4	7.3	98.6
3	n-Propanol	ZrO ₂ /GO	28.3	16.8	59.4
4	Iso-propanol	ZrO ₂ /GO	63.2	58.6	92.7
5	Iso-butanol	ZrO ₂ /GO	42.9	24.8	97.8
6	tert-Butanol	ZrO ₂ /GO	5.8	0	0
7	Iso-propanol	GO	10.6	-	_
8	Iso-propanol	_	3.5	-	_
9	Iso-propanol	ZrO_2	43.2	41.0	94.9

^a Reaction conditions: ethyl levulinate (1 mmol), ZrO₂/GO (20 mg), solvent (10 mL), 180 °C, 3 h

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corresponding the carbonyl compounds. Therefore, *iso*propanol was the best solvent and hydrogen donor for the transfer hydrogenation of ethyl levulinate into GVL over the ZrO_2/GO catalyst.

Furthermore, the transfer hydrogenation of ethyl levulinate into GVL was also performed in the presence of GO. However, no GVL was produced in the presence of GO after 3 h at 180 °C (Table 1, Entry 7). These results clearly indicated that the Lewis acid site of Zr was the active site for the transfer hydrogenation of ethyl levulinate to GVL with alcohols as the hydrogen donor. However, a low conversion of ethyl levulinate in 10.6% was also observed after 3 h at 180 °C in the presence of GO (Table 1, Entry 7). A control experiment was also performed in the absence of GO or ZrO₂/GO, which still gave a very low ethyl levulinate conversion of 3.5% (Table 1, Entry 8). The product was identified to be iso-propyl levulinate either in the presence of GO or without any catalyst. The higher conversion of ethyl levulinate in the presence of GO suggested that GO demonstrated the catalytic activity towards the transesterification, because of the acidic groups such as hydroxyl-, carboxylic acid groups to activate the ester group in ethyl levulinate (Table 1, Entries 7 vs. 8). Furthermore, catalytic transfer hydrogenation of ethyl levulinate to GVL was also carried out in the presence of ZrO₂ at 180 °C. Although GVL was obtained in a high selectivity, the conversion of ethyl levulinate in the presence of ZrO₂ was much lower than that in the presence of ZrO₂/GO (Table 1, Entry 9). The higher conversion of ethyl levulinate over the ZrO₂/GO catalyst in comparison with bulk ZrO₂ should be that ZrO₂ particles were homogeneously dispersed on the surface of GO, and thus much more active sites of ZrO₂ were exposed, resulting a higher reaction rate. In addition, as discussed above, the acidic groups in GO should also play a role in accelerating the transfer hydrogenation of ethyl levulinate into GVL, as the acidic sites in GO can activate the carbonyl group in ethyl levulinate.

3.2 Catalytic Transfer Hydrogenation of Ethyl Levulinate at Different Temperatures

With *iso*-propanol as the best hydrogen donor for the transfer hydrogenation of ethyl levulinate into GVL over the $ZrO_2/$ GO catalyst, the reaction conditions were further optimized in order to get the high yield of GVL. First, the effect of the reaction temperature on the transfer hydrogenation of ethyl levulinate with *iso*-propanol was studied over the ZrO_2/GO catalyst, and the results are shown in Fig. 5. It was found that the reaction temperature showed a great effect on the conversion of ethyl levulinate, but the selectivity of GVL was not greatly influenced by the reaction temperature. Ethyl levulinate conversion greatly increased from 5.8% at a low temperature of 120 °C to 80.6% at 200 °C after



Fig. 5 The effect of the reaction temperature on the transfer hydrogenation of ethyl levulinate. Reaction conditions: ethyl levulinate (1 mmol), ZrO_2/GO (20 mg), *iso*-propanol (10 mL), 3 h

3 h (Fig. 5). These results suggested that an increase of the reaction temperature accelerated the dehydrogenation of *iso*-propanol and the followed hydrogenation of ethyl levulinate into GVL. Nevertheless, the selectivity of GVL remained at a high level in the range from 92.7 to 96.4%. The high selectivity of GVL was possibly due to the flowing reasons as described above. On the one hand, the transesterification of ethyl levulinate with *iso*-propanol was difficult due to the steric hindrance at different reaction temperatures. On the other hand, GVL was stable in our reaction system even at the high temperature of 200 °C.

Furthermore, the kinetics of the transfer hydrogenation of ethyl levulinate over the ZrO₂/GO catalyst was studied. Kinetic experiments on the transfer hydrogenation of ethyl levulinate were performed at three different temperatures of 140, 150 and 160 °C. In our reaction system, iso-propanol is used as the reaction solvent, so it was in large excess. Therefore, the reaction kinetics of the transfer hydrogenation of ethyl levulinate should not be affected by the concentration of iso-propanol. Hence, the transfer hydrogenation of ethyl levulinate can be considered as a pseudo first order reaction to the substrate of ethyl levulinate. Figure 6 depicts the plot of $\ln(C_t/C_0)$ versus time for the transfer hydrogenation of ethyl levulinate over the ZrO2/GO catalyst, in which C_0 is the initial concentration of ethyl levulinate, and C_t represents the concentration of ethyl levulinate at certain reaction time point. As shown in Fig. 6, the pseudo-first order kinetics were observed for the transfer hydrogenation of ethyl levulinate into GVL at three different reaction temperatures. The reaction rate constants for the transfer hydrogenation of ethyl levulinate were determined to be 0.02722, 0.12425 and 0.17532 h⁻¹ for the temperatures of 140, 150 and 160 °C, respectively. The variation of the rate constant (k) with temperature was inserted in Fig. 6. According to



Fig. 6 The reaction kinetics for the hydrogenation of ethyl levulinate to GVL at different temperatures. Reaction condition: the ZrO_2/GO catalyst (20 g), temperature (413–453 K), ethyl levulinate (1 mmol), speed of agitation (1000 rpm), *iso*-propanol (10 mL)

the Arrhenius plot, the activation energy (Ea) was calculated to be 47.69 kJ mol⁻¹ over the ZrO₂/GO catalyst for the transfer hydrogenation of ethyl levulinate into GVL by *iso*-propanol. There were few studies on the calculation of activation energy for transfer hydrogenation of ethyl levulinate into GVL by *iso*-propanol.

3.3 Effect of Catalyst Loading on the Catalytic Transfer Hydrogenation

Then the effect of the catalyst loading on the transfer hydrogenation of ethyl levulinate into GVL was studied at the reaction temperature of 180 °C, and the results are shown in Fig. 7. A general trend was observed as follows: the higher the loading of the ZrO₂/GO catalyst was, the higher the conversion of ethyl levulinate was. The higher ethyl levulinate conversion with the higher loading of the ZrO₂/GO catalyst was due to the presence of much more catalytic sites, which accelerated the transfer hydrogenation of ethyl levulinate to GVL. Interestingly, the effect of the catalyst loading on ethyl levulinate conversion at a low content showed a much more distinct effect than that at high loading range. For example, the conversion of ethyl levulinate greatly increased from the 33.9% with 10 mg of the ZrO₂/GO catalyst to 63.2% with 20 mg of the ZrO₂/GO catalyst. Then it gradually increased from 63.2% with 20 mg of the ZrO₂/GO catalyst to 93.4% with 50 mg of the ZrO₂/GO catalyst. This is due to the fact that the concentration of the substrates on the active sites of the ZrO₂/GO catalyst was much higher with the lower loading than that with a higher loading of the catalysts. Therefore, the increasing trend of the ethyl levulinate conversion became weaker at a high catalyst loading range. However, the selectivity of GVL remained stable around 90%. The stable selectively of ethyl levulinate revealed the catalyst loading have no great effect on the catalyst selectivity, and the selectivity was influenced by other important parameters as discussed above such as the type of alcohols.

Furthermore, the time course of the transfer hydrogenation of ethyl levulinate into GVL was studied at the reaction temperature of 180 °C with the ZrO₂/GO catalyst loading of 20 mg. As depicted in Fig. 8, the molar percentage ethyl levulinate gradually decreased during the reaction process, while the molar percentage of GVL gradually increased. As shown in Fig. 8, the conversion rate of ethyl levulinate was much sharper at an early reaction stage than the latter reaction stage. The reason should be that a higher concentration of ethyl levulinate at an early reaction stage resulted in



Fig. 7 Effect of the catalyst amount on the transfer hydrogenation of ethyl levulinate. Reaction condition: ethyl levulinate (1 mmol), speed of agitation (1000 rpm), *iso*-propanol (10 mL), 180 °C and 3 h



Fig. 8 Time course of the transfer hydrogenation of ethyl levulinate into γ -GVL. Reaction conditions: ethyl levulinate (1 mmol), ZrO₂/GO (20 mg), *iso*-propanol (10 mL), and 180 °C







Fig. 9 The stability of the ZrO_2/GO on the transfer hydrogenation of ethyl levulinate into γ -GVL. Reaction conditions: ethyl levulinate (1 mmol), ZrO_2/GO (20 mg), *iso*-propanol (10 mL), 180 °C and 6 h

a higher reaction rate. During the whole reaction process, the selectivity of GVL remained around 92%. Besides the byproduct generated from the transesterification of ethyl levulinate with *iso*-propanol. No other products were observed during the reaction process as determined by gas chromatography. It has been generally accepted that a product from the hydrogenation of carbonyl group in ethyl levulinate is the intermediate during the transformation of ethyl levulinate into GVL (Scheme 1). However, this intermediate was not detected during the reaction process, suggesting it was not stable, which fast underwent the cyclisation/lactonization to generate the aim product of a stable five-member ring product of GVL.

The long-term stability and reusability of a heterogeneous catalyst are of great importance for the practical application to reduce the manufacturing cost. Hence, the stability of the ZrO_2/GO catalyst was studied. The catalytic transfer hydrogenation of ethyl levulinate into GVL was used as the model reaction to study the recycling experiments of the ZrO_2/GO , which was performed at 180 °C. After reaction, the ZrO_2/GO , which was separated from the reaction mixture by centrifugation, so as to avoid the loss of the weight of the ZrO_2/GO catalyst. The spent catalyst was subsequently washed with water and ethanol, respectively. Then the spent catalyst was dried in a vacuum oven at 80 °C. The spent ZrO_2/GO catalyst was carried out under the identical conditions with the first run. These steps were repeated for five runs. As shown in Fig. 9, the conversion of the ethyl levulinate

Fig. 10 The stability of the ZrO_2/GO on the transfer hydrogenation of ethyl levulinate into γ -GVL. Reaction conditions: ethyl levulinate (1 mmol), ZrO_2/GO (20 mg), *iso*-propanol (10 mL), 180 °C and 3 h

and the selectivity of GVL were almost the same for the six runs. These results indicated that the as-prepared ZrO_2/GO catalyst was stable during the reaction process without the loss of its catalytic activity.

Furthermore, a hot filtration experiment was also conduct to further confirm the high stability of the ZrO_2/GO catalyst. After the reaction for 3 h at 180 °C, the ZrO_2/GO catalyst was removed. Then the liquid solution was continuously to be heated at 180 °C for 10 h. As shown in Fig. 10, the conversion of GVL remained stable without any increase, which further confirmed that the ZrO_2/GO catalyst was highly stable during the reaction process without the leach of the active sites into the reaction solution. All of the results confirmed that our transfer hydrogenation of ethyl levulinate into GVL was a real heterogeneous reaction.

4 Conclusion

In conclusion, we have developed a new method for the transfer hydrogenation of biomass-derived ethyl levulinate into GVL using *iso*-propanol as the hydrogen donor via a tandem MPV reduction and cyclisation/lactonization over a non-noble catalyst. The ZrO_2/GO catalyst can be simply prepared via the hydrothermal treatment of $ZrOCl_2 \cdot 8H_2O$ in the presence of GO, and the as-prepared ZrO_2/GO demonstrated high activity towards the transfer hydrogenation of ethyl levulinate for the GVL production. Various parameters

were optimized for the transfer hydrogenation of ethyl levulinate into GVL. It was found the structure of hydrogen donors showed a great effect on the ethyl levulinate conversion as well as the GVL selectivity. *Iso*-propanol was observed to be the best hydrogen donor, which produced the highest selectivity of GVL. A full conversion of ethyl levulinate and a high selectivity of GVL of 94.8% were obtained at the reaction temperature of 180 °C for 10 h by the use of 20 mg of the ZrO₂/GO catalyst. Kinetic studies indicated that the transfer hydrogenation of ethyl levulinate into GVL was sensitive to the reaction temperature with activation energy of 47.69 kJ mol⁻¹. The ZrO₂/GO catalyst was highly stable and could be reused for several times without the loss of its catalytic activity.

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Affiliations

Jinhua Lai¹ · Shuolin Zhou¹ · Xianxiang Liu¹ · Yongjun Yang² · Jing Lei² · Qiong Xu¹ · Dulin Yin¹

- ¹ National & Local Joint Engineering Laboratory for New Petro-Chemical Materials and Fine Utilization of Resources, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha 410081, People's Republic of China
- ² Chenzhou Gao Xin Material Co., Ltd., Chenzhou 423000, Hunan, People's Republic of China